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The Preparation of Different Types of Polynuclear Transition Metal-Sulfur Compounds by Thiometallates, Including Cubane-like Ones. Crystal Structures of $\{Cu_3WS_3Cl\}(PPh_3)_3S$, $\{Cu_3WS_3Cl\}(PPh_3)_3O$, $\{Cu_3MoS_3Cl\}(PPh_3)_3S$, $\{Cu_3MoS_3Cl\}(PPh_3)_3O$, $(PPh_3)_3Cu_2WS_4 \cdot 0.8CH_2Cl_2$ and $(PPh_3)_3Ag_2MoS_4 \cdot 0.8CH_2Cl_2$

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The following compounds have been prepared by reaction of aqueous solutions of MS_4^{2-} *and* MOS_3^{2-} *(M = Mo, W) with dichloromethane solutions of* $CuCl_2 \cdot 2H_2O$ *(or* $AgNO_3$*) and* PPh_3*:* $\{Cu_3WS_3Cl\}(PPh_3)_3S$ *(I),* $\{Cu_3WS_3Cl\}(PPh_3)_3O$ *(II),* $\{Cu_3MoS_3Cl\}(PPh_3)_3S$ *(III),* $\{Cu_3MoS_3Cl\}(PPh_3)_3O$ *(IV),* $(PPh_3)_3Cu_2WS_4 \cdot 0.8CH_2Cl_2$ *(V) and* $(PPh_3)_3Ag_2MoS_4 \cdot 0.8CH_2Cl_2$ *(VI). The crystal and molecular structures of I–VI were determined from single crystal X-ray diffractometer data. I–IV crystallize in the orthorhombic space group* $P2_12_12_1$ *with four molecules in the unit cell (I:* a = *13.002(2),* b = *17.851(2),* c = *22.682(2)* Å, V = *5264.2* Å^3, d_{calcd} = *1.67 g* cm^{-3}*; II:* a = *12.825(2),* b = *17.529(4),* c = *22.711(4)* Å, V = *5105.5* Å^3, d_{calcd} = *1.70 g* cm^{-3}*; III:* a = *12.991(2),* b = *17.833(2),* c = *22.674(3)* Å, V = *5253.1* Å^3, d_{calcd} = *1.56 g* cm^{-3}*; IV:* a = *12.839(2),* b = *17.553(3),* c = *22.761(3)* Å, V = *5129.5* Å^3, d_{calcd} = 1.58 g cm^{-3}*). The structures were refined to final R values of 0.063 (I), 0.071 (II), 0.063 (III) and 0.062 (IV) for 5073 (I), 5349 (II), 3537 (III) and 3016 (IV) independent data. The structure can be described as a strongly distorted cube, four corners being formed by the* MS_4^{2-} *or* MOS_3^{2-} *ligand (with a terminal S or O atom). The remaining corners are occupied by one chlorine and three copper atoms (with one* PPh_3 *ligand bonded to each of the latter).*

V and VI crystallize in the monoclinic space group $P2_1/c$ *with four molecules in the unit cell (V:* a = *18.372(6),* b = *16.702(7),* c = *17.740(8)* Å, β = *95.56(3)*°, V = *5417.9* Å^3, d_{calcd} = *1.50 g* cm^{-3}*; VI:* a = *18.154(4),* b = *17.322(3),* c = *17.790(3)* Å, β = *95.11(2)*°, V = *5572.0* Å^3, d_{calcd} = *1.46 g* cm^{-3}*. The structures were refined to final R factors of 0.109 (V) and 0.084 (VI) for 4844 and 5590 independent reflections respectively.*

V and VI have a structure with a doubly bridging MS_4^{2-} *ligand, generating a nearly linear* $M' \cdots M \cdots M'{-}P$ *moiety with one tetrahedrally and one trigonally planar-coordinated M' (M' = Cu, Ag) atom.*

The generation of different types of polynuclear compounds by thiometallates containing Cu^+ *and* Ag^+ *(including those with the biometals Cu and Mo) and the bioinorganic relevance is discussed.*

Introduction

The biological relevance of polynuclear transition metal sulfur complexes with different biometals (like Fe, Cu, Mo) is well known. Those containing Fe, S and Mo are interesting with respect to the active sites of nitrogenase [1], and those containing Cu and Mo because of the interrelation between these metals in numerous biological processes [2–7] (the so called Mo–Cu antagonism [2]). Thiometallates like MoS_4^{2-} and WS_4^{2-} [8–10] can be used as 'synthons' for the generation of several novel types of polynuclear transition metal compounds with ring (*e.g.* the novel eight membered pure metal sulfur system $[S_2\{WS_2Au_2S_2W\}S_2]^{2-}$) [11], cluster and cage systems [12–15], depending on the type of thiometallate, the transition metal coordination centre and the ligands. The metallates act as bi-, tri- and terdentate ligands and have low-lying unoccupied orbitals. The trimetallic thioheteroanions [8, 16, 17] like $[Co(WS_4)_2]^{2-}$, $[Ni(WS_4)_2]^{2-}$, $[Ni(WOS_3)_2]^{2-}$ and $[Ni(WO_2S_2)_2]^{2-}$ are remarkable as they show reversible reduction processes [18, 19]. This property has been explained for $[Co(WS_4)_2]^{2-}$ to be due to the existence of delocalized molecular orbitals [19].

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Several different structural types of polynuclear complexes can be obtained with the soft acids Cu^+ and Ag^+ and thiometallates in the presence of other ligands like PPh_3. In this paper compounds obtained from Cu^{2+} and MoS_4^{2-} are also reported, compounds which are especially interesting because a Cu^{2+}/MoS_4^{2-} interaction has been claimed to be responsible for the Mo–Cu antagonism in biological processes (thiomolybdates are the most effective antagonists of copper causing a secondary trace element deficiency [7]). The generation of different types of polynuclear transition metal sulfur compounds generated from MS_4^{2-} and MOS_3^{2-} (M = Mo, W) will be discussed.

Experimental

Preparation of $\{Cu_3WS_3Cl\}(PPh_3)_3S$ (I)

An aqueous solution (100 ml) of 0.22 g (~0.6 mmol) $(NH_4)_2WS_4$ was extracted with a dichloromethane solution (25 ml) of 0.17 g (~1 mmol) $CuCl_2 \cdot 2H_2O$ and 0.4 g (~1.5 mmol) PPh_3. (It was essential to stir the two phase system less than 1 min as otherwise a high amount of V was formed). After topping the filtered organic phase with a mixture of n-pentane (50 ml) and acetone (10 ml) in a narrow tube (to avoid mixing of the phases) yellow rhombohedral crystals (0.19 g) of I were obtained at the walls of the tube after 2–3 days. (Ra: $\nu(W-S)_{term}$, 513; ir: $\nu(W-S)_{br}$, 436 cm^{-1}). *Anal.* Calcd. for $C_{54}H_{45}ClCu_3P_3S_4W$: C, 48.95; Cl, 2.68; Cu, 14.39; S, 9.68. Found: C, 49.08; Cl, 2.5; Cu, 14.5; S, 9.6.

Preparation of $\{Cu_3WS_3Cl\}(PPh_3)_3O$ (II)

II was prepared in the same way as I with 0.35 g (~0.6 mmol) Cs_2WOS_3 instead of $(NH_4)_2WS_4$. Yield: 0.1 g of yellow rhombohedral crystals. (ir: $\nu(W-O)$, 929; $\nu(W-S)_{br}$, 436 cm^{-1}). *Anal.* Calcd. for $C_{54}H_{45}ClCu_3OP_3S_3W$: C, 49.55; Cl, 2.71; Cu, 14.56; S, 7.35. Found: C, 49.38; Cl, 2.7; Cu, 14.9; S, 7.2.

Preparation of $\{Cu_3MoS_3Cl\}(PPh_3)_3S$ (III)

An aqueous solution (100 ml) of 0.13 g (~0.5 mmol) $(NH_4)_2MoS_4$ was extracted (less than 1 min) with a dichloromethane solution (25 ml) of 0.17 g (~1 mmol) $CuCl_2 \cdot 2H_2O$ and 0.4 g (~1.5 mmol) PPh_3. III precipitated in crystalline form in a tube containing the filtered organic phase which was kept for 2–3 days in a closed beaker containing diethylether (change of solubility via vapor diffusion). Small impurities of red platelets of $(PPh_3)_3Cu_2MoS_4 \cdot 0.8CH_2Cl_2$ [27] could be separated mechanically. Yield: 0.14 g of red rhombohedral crystals. (Ra: $\nu(Mo-S)_{term}$, 515/527; ir: $\nu(Mo-S)_{br}$, 441/447 cm^{-1}). *Anal.* Calcd. for $C_{54}H_{45}ClCu_3MoP_3S_4$: C, 52.43; Cl, 2.87; Cu, 15.41; S, 10.37. Found: C, 52.18; Cl, 2.7; Cu, 15.6; S, 10.5.

Preparation of $\{Cu_3MoS_3Cl\}(PPh_3)_3O$ (IV)

IV was prepared in the same way as I with 0.23 g (~0.5 mmol) Cs_2MoOS_3 (n-pentane–acetone ratio: 2:1). Yield: 0.1 g of red rhombohedral crystals. (ir: $\nu(Mo-O)$, 908; $\nu(Mo-S)_{br}$, 444/451 cm^{-1}). *Anal.* Calcd. for $C_{54}H_{45}ClCu_3MoOP_3S_3$: C, 53.12; Cl, 2.90; Cu, 15.61; S, 7.88. Found: C, 53.33; Cl, 2.8; Cu, 15.7; S, 7.7.

Preparation of $(PPh_3)_3Cu_2WS_4 \cdot 0.8CH_2Cl_2$ (V)

V was prepared in the same way as I with 0.35 g (~1 mmol) $(NH_4)_2WS_4$ and 0.47 g (~1.8 mmol) PPh_3 but the two phase system was stirred for at least 3 minutes. Yield: 0.26 g of yellow platelets. (ir: $\nu(W-S)_{br}$, 451/455 cm^{-1}). *Anal.* Calcd. for $C_{54}H_{45}Cu_2P_3S_4W \cdot 0.8CH_2Cl_2$: C, 50.87; Cl, 4.38; S, 9.91. Found: C, 50.95; Cl, 4.3; S, 9.8.

Preparation of $(PPh_3)_3Ag_2MoS_4 \cdot 0.8CH_2Cl_2$ (VI)

VI was prepared in the same way as I with 0.22 g (~0.8 mmol) $(NH_4)_2MoS_4$, 0.21 g (~1.2 mmol) $AgNO_3$ and 1.1 g (~4.2 mmol) PPh_3 (stirring time: 3 minutes). Acetone/pentane ratio: 1:11. Yield: 0.33 g of red platelets. (ir: $\nu(Mo-S)_{br}$, 458/467 cm^{-1}). *Anal.* Calcd. for $C_{54}H_{45}Ag_2MoP_3S_4 \cdot 0.8CH_2Cl_2$: C, 50.84; Cl, 4.38; S, 9.90. Found: C, 50.52; Cl, 4.1; S, 10.6.

Infrared spectra (only most intense bands are given) were recorded on a Perkin Elmer Model 180 Spectrophotometer using KBr pellets. In the case of the compounds I and III the band due to $\nu(M-S)_{term}$ is overlapped by a band of the PPh_3 ligand. (The corresponding Raman bands were recorded on a Spex Ramanlog V spectrometer ($\lambda_e = 647.1$ nm)).

X-Ray Structure Determination [20]

The molecular structures of I–VI were determined by single crystal X-ray structure analyses.

A summary of the crystal data and details concerning the intensity data collection are given in Table I. The unit cell parameters were obtained (at 21 °C) by a least squares refinement of the angular settings of 9–12 high-angle reflections. Intensity data were collected on a Syntex $P2_1$ four-circle diffractometer. An empirical absorption correction was applied for I and II [20]. The data were corrected for Lorentz and polarization effects. The W, Mo, Ag and Cu atoms were located from a three-dimensional Patterson synthesis. The positional parameters of the non-hydrogen atoms were deduced from successive difference-Fourier syntheses. Several cycles converged at $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.063$(I), 0.071(II), 0.063(III), 0.062(IV), 0.109(V), 0.084(VI) and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2} = 0.062$(I),

TABLE I. Crystal and Intensity Collection Data.

a. Summary of Crystal Data and Intensity Collection for I–III

Crystal Data

compound	$\{Cu_3WS_3Cl\}(PPh_3)_3S$	$\{Cu_3WS_3Cl\}(PPh_3)_3O$	$\{Cu_3MoS_3Cl\}(PPh_3)_3S$
empirical formula	$C_{54}H_{45}ClCu_3P_3S_4W$	$C_{54}H_{45}ClCu_3OP_3S_3W$	$C_{54}H_{45}ClCu_3MoP_3S_4$
Fw	1325.05	1308.99	1237.15
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a, Å	13.002(2)	12.825(2)	12.991(2)
b, A	17.851(2)	17.529(4)	17.833(2)
c, A	22.682(2)	22.711(4)	22.674(3)
V, Å^3	5264.2	5105.5	5253.1
d_{calcd}, g cm^{-3}	1.67	1.70	1.56
Z	4	4	4
crystal dimensions, mm	0.4 × 0.35 × 0.35	0.4 × 0.35 × 0.2	0.3 × 0.3 × 0.2
absorption coefficient μ(Mo-K$_\alpha$), cm^{-1}	38.7	39.6	18.0
F(000), electrons	2624	2592	2496

Data collection

scan mode	ω	$\theta - 2\theta$	ω
scan range (2θ), °	4–54	4–54	4–48
scan width	1° in ω bisected by K$_{\alpha1,2}$ maximum	1° below K$_{\alpha1}$ to 1° above K$_{\alpha2}$ in 2θ	1° in ω bisected by K$_{\alpha1,2}$ maximum
scan speed, °/min	3.45–29.3	3.91–29.3	3.45–29.3
background scan time ratio	0.75	0.7	0.75
check reflections	1 reflection every 50 reflections		
no. of observed reflections	6330	6165	4569
no. of observed reflections ($I \geq 1.96\sigma(I)$)	5073	5349	3537
no. of variables	325	320	325

b. Summary of Crystal Data and Intensity Collection for IV–VI

Crystal Data

Compound	$\{Cu_3MoS_3Cl\}(PPh_3)_3O$	$(PPh_3)_3Cu_2WS_4 \cdot 0.8CH_2Cl_2$	$(PPh_3)_3Ag_2MoS_4 \cdot 0.8CH_2Cl_2$
empirical formula	$C_{54}H_{45}ClCu_3MoOP_3S_3$	$C_{54}H_{45}Cu_2P_3S_4W \cdot 0.8CH_2Cl_2$	$C_{54}H_{45}Ag_2MoP_3S_4 \cdot 0.8CH_2Cl_2$
Fw	1221.08	1294.00	1294.74
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a, A	12.839(2)	18.372(6)	18.154(4)
b, A	17.553(3)	16.702(7)	17.322(3)
c, A	22.761(3)	17.740(8)	17.790(3)
β, °	90.0	95.56(3)	95.11(2)
V, Å^3	5129.5	5417.9	5572.0
d_{calcd}, g cm^{-3}	1.58	1.50	1.46
Z	4	4	4
crystal dimensions, mm	0.25 × 0.3 × 0.3	0.12 × 0.3 × 0.8	0.15 × 0.45 × 0.6

(continued overleaf)

TABLE I. *(continued)*

absorption coefficient μ(Mo-Kα), cm^{-1}	18.1	33.2	11.6
F(000), electrons	2464	2440	2456
Data collection			
scan mode	ω	ω	ω
scan range (2θ), °	4–46	4–44	4–44
scan width	1° in ω bisected by K$\alpha_{1,2}$ maximum	1° in ω bisected by K$\alpha_{1,2}$ maximum	1° in ω bisected by K$\alpha_{1,2}$ maximum
scan speed, °/min	3.45–29.3	3.45–29.3	3.45–29.3
background scan time ratio	0.75	0.75	0.75
check reflections	1 reflection every 50 reflections		
no. of measured reflections	3981	6895	7076
no. of observed reflections ($I \geq 1.96\sigma(I)$)	3016	4844	5590
no. of variables	217	315	319

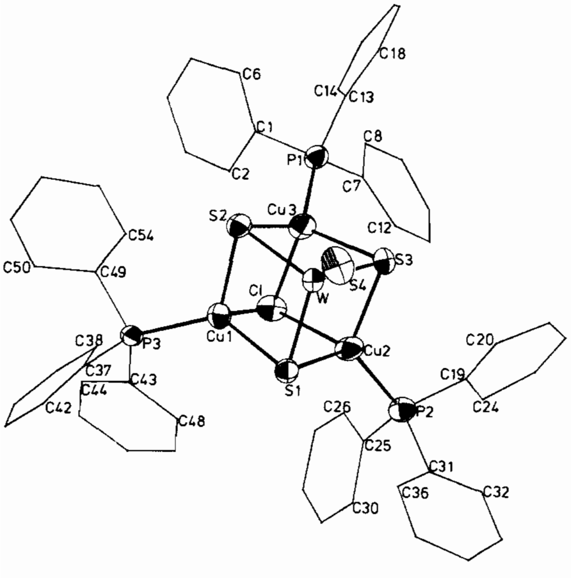

Fig. 1. Molecular structure of $\{Cu_3WS_3Cl\}(PPh_3)_3S$.

0.069(II), 0.054(III), 0.059(IV), 0.114(V), 0.103(VI) ($1/w = \sigma^2(F_o)^2$), respectively. Because of the noncentrosymmetric space group of I–IV their structures were also refined having inverted all positional parameters. But as the corresponding residuals were R = 0.083(I), 0.090(II), 0.070(III), 0.067(IV) and R_w = 0.087(I), 0.087(II), 0.061(III), 0.064(IV) the original set was chosen as the correct one. Anomalous dispersion corrections [21] were applied to the W, Mo, Ag, Cu, Cl and S atoms in all cases.

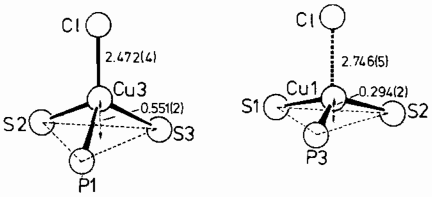

Fig. 2. Different types of Cu-coordination polyhedra in compounds I–IV. (Numerical values are given for I).

The temperature factors for the W, Mo, Ag, Cu, Cl, S and P atoms were treated in the anisotropic form. In the final stage of refinement no parameter shifted more than 0.15σ, where σ is the standard deviation of the parameter.

The atomic scattering factors for W, Mo, Ag, Cu, Cl, S, P, O and C were taken from ref. [21]. The final ΔF maps contained no significant peaks.

The positional and thermal parameters of I and VI are given in Table II. Those of II–V are available as supplementary material [22].

Results and Discussion

The structures of the isomorphous compounds I–IV consist of one molecule in the asymmetric unit. The interatomic distances and bond angles are listed in Table III.

The central unit of I–IV can be described as a strongly distorted cube in which four corners are occupied by one Cl and three Cu atoms (with a PPh_3 ligand being bonded to each Cu). The cube is

TABLE II. Positional and Thermal Parameters.

a. Positional and Thermal (Å^2)^a Parameters for $\{Cu_3WS_3Cl\}(PPh_3)_3S$ with Standard Deviations.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	0.1688(1)	0.4963(1)	0.5225(1)	2.10(2)	2.09(2)	2.61(2)	−0.05(3)	0.30(2)	0.11(3)
Cu1	0.3477(2)	0.4212(1)	0.5328(1)	3.64(10)	4.18(9)	3.02(9)	1.64(8)	0.02(8)	−0.26(8)
Cu2	0.3031(2)	0.5945(1)	0.5724(1)	4.47(11)	2.89(9)	3.04(8)	−0.99(8)	−0.77(8)	−0.23(8)
Cu3	0.3052(2)	0.5452(1)	0.4393(1)	4.13(10)	3.12(9)	2.55(8)	−0.31(8)	0.87(8)	0.37(7)
S1	0.2565(3)	0.4773(2)	0.6073(2)	3.66(19)	2.82(19)	2.27(16)	0.39(15)	0.73(14)	0.32(13)
S2	0.2401(3)	0.4237(2)	0.4522(2)	3.26(19)	2.58(16)	3.04(18)	−0.42(15)	−0.38(14)	−0.30(14)
S3	0.1898(3)	0.6160(2)	0.4957(2)	2.88(18)	2.20(14)	3.35(17)	0.12(14)	0.04(14)	0.11(13)
S4	0.0094(3)	0.4719(3)	0.5331(2)	2.63(18)	4.61(22)	6.58(29)	−0.76(16)	0.85(20)	1.00(21)
P1	0.3512(3)	0.5969(2)	0.3546(2)	3.29(21)	2.63(17)	2.35(16)	−0.09(17)	0.35(15)	−0.07(14)
P2	0.3622(3)	0.6872(3)	0.6275(2)	3.19(21)	3.16(20)	3.08(19)	−0.64(17)	−0.17(16)	−0.16(17)
P3	0.4731(3)	0.3367(2)	0.5357(2)	2.34(17)	3.15(18)	1.99(17)	0.64(15)	−0.08(14)	−0.02(14)
Cl	0.4584(3)	0.5468(2)	0.5038(2)	2.76(17)	4.21(20)	3.18(17)	−0.48(17)	−0.02(14)	0.22(15)

Atom	x	y	z	B	Atom	x	y	z	B
C1	0.4499(12)	0.5492(9)	0.3118(6)	3.1(3)	C28	0.7128(16)	0.6657(11)	0.6575(9)	5.4(5)
C2	0.5438(16)	0.5409(11)	0.3393(8)	5.6(5)	C29	0.6464(17)	0.6614(12)	0.7045(9)	6.1(5)
C3	0.6284(16)	0.5123(12)	0.3044(9)	6.0(5)	C30	0.5358(15)	0.6670(11)	0.7014(8)	4.8(4)
C4	0.6168(16)	0.4902(13)	0.2476(9)	6.5(5)	C31	0.3077(12)	0.6963(8)	0.7050(6)	2.8(3)
C5	0.5190(16)	0.4929(12)	0.2213(8)	5.7(5)	C32	0.2902(15)	0.7648(10)	0.7288(8)	4.7(4)
C6	0.4332(15)	0.5284(10)	0.2512(8)	5.0(4)	C33	0.2554(17)	0.7729(12)	0.7862(9)	5.9(5)
C7	0.4146(11)	0.6894(8)	0.3641(6)	2.2(3)	C34	0.2242(15)	0.7060(11)	0.8150(9)	5.0(4)
C8	0.4739(12)	0.7230(9)	0.3169(7)	3.2(3)	C35	0.2332(13)	0.6347(10)	0.7897(7)	3.7(4)
C9	0.5177(13)	0.7933(10)	0.3258(8)	4.3(4)	C36	0.2729(13)	0.6318(10)	0.7283(8)	4.0(4)
C10	0.5138(14)	0.8251(11)	0.3808(8)	4.8(4)	C37	0.4453(12)	0.2465(8)	0.5761(7)	3.0(3)
C11	0.4511(12)	0.7951(9)	0.4269(7)	3.0(3)	C38	0.3420(17)	0.2282(11)	0.5714(9)	5.7(5)
C12	0.4033(13)	0.7259(9)	0.4187(7)	3.7(4)	C39	0.3202(15)	0.1572(10)	0.6024(7)	4.5(4)
C13	0.2406(13)	0.6075(9)	0.3059(7)	3.4(3)	C40	0.3936(14)	0.1151(10)	0.6287(8)	4.1(4)
C14	0.1590(16)	0.5640(10)	0.3132(7)	4.7(4)	C41	0.4995(15)	0.1406(11)	0.6348(9)	5.1(5)
C15	0.0635(19)	0.5699(13)	0.2774(10)	6.7(5)	C42	0.5199(13)	0.2096(9)	0.6045(7)	3.5(3)
C16	0.0680(17)	0.6265(12)	0.2348(9)	5.8(5)	C43	0.5914(12)	0.3732(9)	0.5662(7)	3.0(3)
C17	0.1501(20)	0.6674(14)	0.2217(11)	8.2(7)	C44	0.6890(14)	0.3418(10)	0.5487(7)	4.6(4)
C18	0.2361(16)	0.6617(12)	0.2574(10)	6.0(5)	C45	0.7784(18)	0.3667(13)	0.5714(10)	7.0(6)
C19	0.3428(12)	0.7823(8)	0.5945(6)	2.7(3)	C46	0.7752(15)	0.4327(11)	0.6099(8)	5.2(5)
C20	0.2500(13)	0.7968(10)	0.5713(8)	4.2(4)	C47	0.6812(16)	0.4657(11)	0.6247(8)	5.5(4)
C21	0.2232(14)	0.8699(11)	0.5519(8)	4.5(4)	C48	0.5855(15)	0.4368(11)	0.6062(8)	4.9(4)
C22	0.3120(19)	0.9279(13)	0.5525(9)	7.2(6)	C49	0.5092(12)	0.3067(9)	0.4602(7)	3.0(3)
C23	0.4000(14)	0.9112(10)	0.5756(8)	4.8(4)	C50	0.5415(14)	0.2292(10)	0.4507(7)	4.1(4)
C24	0.4246(15)	0.8366(11)	0.6029(8)	4.7(4)	C51	0.5650(15)	0.2115(10)	0.3956(8)	4.6(4)
C25	0.5014(11)	0.6795(8)	0.6401(7)	2.7(3)	C52	0.5584(15)	0.2627(10)	0.3487(8)	4.7(4)
C26	0.5700(16)	0.6823(11)	0.5962(8)	5.3(5)	C53	0.5331(13)	0.3375(9)	0.3617(7)	3.4(3)
C27	0.6714(16)	0.6771(11)	0.5995(8)	5.2(4)	C54	0.5083(14)	0.3593(10)	0.4179(8)	4.2(4)

b. Positional and Thermal (Å^2)^a Parameters for $(PPh_3)_3Ag_2MoS_4 \cdot 0.8CH_2Cl_2$ with Standard Deviations.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.2291(1)	0.4159(1)	0.1881(1)	3.62(7)	1.57(6)	3.62(7)	0.22(5)	0.91(6)	0.00(5)
Ag1	0.2156(1)	0.2415(1)	0.1877(1)	3.36(6)	2.05(5)	4.00(6)	0.24(5)	0.06(5)	0.13(5)
Ag2	0.2457(1)	0.5800(1)	0.1869(1)	5.90(8)	1.66(5)	5.18(7)	−0.14(5)	1.14(6)	−0.04(5)
S1	0.1634(2)	0.3514(2)	0.2647(2)	4.22(23)	2.74(19)	4.00(23)	−0.17(17)	1.91(18)	−0.13(17)
S2	0.1539(3)	0.4944(3)	0.1199(3)	5.70(26)	3.04(21)	3.91(23)	0.80(20)	−0.71(19)	−0.22(18)
S3	0.3165(3)	0.4788(3)	0.2580(3)	3.92(23)	3.41(22)	5.39(26)	−0.82(18)	−0.47(19)	0.50(19)
S4	0.2823(3)	0.3403(2)	0.1098(3)	6.73(30)	2.58(21)	5.87(29)	−0.03(20)	3.89(24)	−0.16(19)
P1	0.3019(2)	0.1659(2)	0.2739(2)	3.23(21)	2.43(20)	3.52(22)	0.31(16)	0.02(17)	0.02(16)

(continued overleaf)

TABLE II. *(continued)*

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P2	0.1259(2)	0.1760(2)	0.0967(2)	3.32(21)	2.35(18)	3.30(21)	−0.38(16)	0.15(16)	0.21(16)
P3	0.2605(3)	0.7164(2)	0.1809(3)	4.10(23)	1.71(17)	4.42(24)	0.12(17)	0.90(19)	0.11(17)

Atom	x	y	z	B	Atom	x	y	z	B
C1	0.2550(9)	0.0958(9)	0.3301(9)	3.5(3)	C29	0.0119(10)	0.0630(11)	0.2518(10)	5.0(4)
C2	0.2050(10)	0.1239(11)	0.3812(10)	4.8(4)	C30	0.0653(9)	0.1093(10)	0.2153(9)	4.1(4)
C3	0.1684(11)	0.0741(11)	0.4265(11)	5.3(4)	C31	0.1714(8)	0.1116(9)	0.0378(8)	3.1(3)
C4	0.1804(11)	−0.0068(12)	0.4155(11)	5.8(5)	C32	0.2142(9)	0.1410(10)	−0.0163(9)	3.9(4)
C5	0.2248(11)	−0.0335(12)	0.3668(11)	6.0(5)	C33	0.2590(11)	0.0926(11)	−0.0569(11)	5.7(5)
C6	0.2632(10)	0.0173(10)	0.3212(10)	4.6(4)	C34	0.2576(10)	0.0112(10)	−0.0464(10)	4.3(4)
C7	0.3678(8)	0.1098(8)	0.2265(8)	2.8(3)	C35	0.2173(12)	−0.0179(12)	0.0112(12)	6.5(5)
C8	0.4304(9)	0.0789(10)	0.2658(10)	4.2(4)	C36	0.1728(10)	0.0292(10)	0.0524(10)	4.8(4)
C9	0.4841(10)	0.0364(10)	0.2258(10)	4.6(4)	C37	0.2690(8)	0.7472(9)	0.0852(9)	3.2(3)
C10	0.4728(10)	0.0264(10)	0.1507(10)	4.8(4)	C38	0.2125(11)	0.7331(11)	0.0350(11)	5.5(5)
C11	0.4093(12)	0.0565(12)	0.1086(12)	6.4(5)	C39	0.2190(12)	0.7506(13)	−0.0428(12)	7.2(6)
C12	0.3581(10)	0.1022(10)	0.1472(10)	4.7(4)	C40	0.2844(11)	0.7896(12)	−0.0631(12)	6.3(5)
C13	0.3604(9)	0.2213(9)	0.3429(9)	3.3(3)	C41	0.3369(12)	0.8123(12)	−0.0096(12)	6.6(5)
C14	0.4004(10)	0.2815(11)	0.3121(10)	5.1(4)	C42	0.3321(11)	0.7895(12)	0.0660(11)	5.7(5)
C15	0.4483(11)	0.3284(11)	0.3622(11)	5.5(5)	C43	0.3389(8)	0.7546(9)	0.2404(9)	3.4(3)
C16	0.4553(11)	0.3142(12)	0.4360(11)	6.1(5)	C44	0.3459(11)	0.8312(11)	0.2573(11)	5.6(5)
C17	0.4158(12)	0.2562(13)	0.4686(12)	6.5(5)	C45	0.4052(11)	0.8601(12)	0.3040(11)	5.7(5)
C18	0.3645(10)	0.2068(11)	0.4209(10)	5.1(4)	C46	0.4616(11)	0.8058(11)	0.3336(11)	5.5(5)
C19	0.0697(8)	0.2403(9)	0.0304(9)	3.3(3)	C47	0.4572(11)	0.7298(11)	0.3142(11)	5.4(5)
C20	0.0474(9)	0.3082(9)	0.0608(9)	3.6(3)	C48	0.3950(10)	0.7020(10)	0.2672(10)	4.5(4)
C21	0.0007(11)	0.3597(11)	0.0164(11)	5.4(5)	C49	0.1811(8)	0.7691(9)	0.2114(8)	3.2(3)
C22	−0.0210(11)	0.3385(11)	−0.0568(11)	5.9(5)	C50	0.1596(9)	0.8430(10)	0.1820(10)	4.3(4)
C23	0.0042(11)	0.2744(12)	−0.0909(11)	5.9(5)	C51	0.1024(11)	0.8790(11)	0.2108(10)	5.3(4)
C24	0.0493(9)	0.2223(10)	−0.0443(9)	4.1(4)	C52	0.0597(9)	0.8477(10)	0.2618(10)	4.2(4)
C25	0.0594(9)	0.1205(9)	0.1380(9)	3.5(3)	C53	0.0771(10)	0.7718(10)	0.2897(10)	4.5(4)
C26	0.0004(11)	0.0808(11)	0.0919(11)	5.4(5)	C54	0.1386(9)	0.7327(10)	0.2629(9)	3.9(4)
C27	−0.0536(12)	0.0379(12)	0.1308(12)	6.5(5)	Cl1	0.3797(17)	0.4932(19)	−0.0061(18)	13.4(9)
C28	−0.0458(11)	0.0317(12)	0.2051(11)	5.8(5)	Cl2	0.4449(12)	0.4647(12)	0.0665(11)	20.3(7)
					Cl3	0.3941(10)	0.5969(10)	0.0544(10)	16.7(6)

[a] The anisotropic temperature factor used is defined as $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

TABLE III. Interatomic Distances and Bond Angles.

a. Interatomic Distances (Å) in I–IV with Standard Deviations.

Atoms	I	II	III	IV
		A. M–Cu and Cu···Cu Distances (M = Mo, W)		
M–Cu1	2.695(2)	2.721(2)	2.678(2)	2.705(2)
M–Cu2	2.721(2)	2.730(2)	2.702(2)	2.710(3)
M–Cu3	2.734(2)	2.763(2)	2.720(2)	2.740(2)
Cu1···Cu2	3.272(3)	3.303(3)	3.270(2)	3.291(3)
Cu1···Cu3	3.116(3)	3.110(3)	3.117(2)	3.104(3)
Cu2···Cu3	3.145(3)	3.216(3)	3.144(2)	3.199(3)

(continued on facing page)

TABLE III. *(continued)*

Atoms	I	II	III	IV
B. M–S, M–X, Cu–S, Cu–Cl and Cu–P Distances (M = Mo, W; X = S4, O)				
M–S1	2.261(4)	2.248(4)	2.269(4)	2.270(5)
M–S2	2.254(4)	2.239(4)	2.253(4)	2.260(5)
M–S3	2.239(4)	2.237(4)	2.241(3)	2.247(4)
M–X	2.131(4)	1.754(11)	2.118(4)	1.769(10)
Cu1–S1	2.294(4)	2.287(5)	2.266(4)	2.280(5)
Cu1–S2	2.303(5)	2.313(5)	2.281(4)	2.291(5)
Cu2–S1	2.317(4)	2.306(5)	2.293(4)	2.278(5)
Cu2–S3	2.312(4)	2.295(5)	2.287(4)	2.277(5)
Cu3–S2	2.346(5)	2.323(5)	2.318(4)	2.314(5)
Cu3–S3	2.343(4)	2.362(5)	2.332(4)	2.322(5)
Cu1–Cl	2.746(5)	2.653(5)	2.764(4)	2.684(5)
Cu2–Cl	2.687(4)	2.744(5)	2.723(4)	2.772(5)
Cu3–Cl	2.472(4)	2.457(5)	2.471(4)	2.471(4)
Cu1–P3	2.223(4)	2.199(5)	2.224(4)	2.227(5)
Cu2–P2	2.212(5)	2.200(5)	2.225(4)	2.220(5)
Cu3–P1	2.213(4)	2.200(5)	2.225(4)	2.211(5)
C. Cl···S and S···S Distances within $\{Cu_3MS_3Cl\}$ core (M = Mo, W)				
Cl···S1	3.735(6)	3.675(6)	3.728(5)	3.690(6)
Cl···S2	3.776(6)	3.711(6)	3.744(5)	3.713(6)
Cl···S3	3.709(6)	3.685(6)	3.703(5)	3.676(6)
S1···S2	3.652(6)	3.616(6)	3.643(5)	3.641(6)
S1···S3	3.646(5)	3.620(6)	3.639(5)	3.630(6)
S2···S3	3.631(5)	3.600(6)	3.625(5)	3.614(6)
D. Mean Values for the PPh_3 Units				
P–C	1.851	1.842	1.832	1.829
C–C	1.406	1.395	1.409	1.395[a]

b. Bond Angles (deg) in I–IV with Standard Deviations

Atoms	I	II	III	IV
A. S–M–S and S–M–X Angles (M = Mo, W; X = S4, O)				
S1–M–S2	107.9(2)	107.4(2)	107.3(1)	107.0(2)
S1–M–S3	108.2(1)	107.7(2)	107.6(1)	106.9(2)
S1–M–X	111.3(2)	111.6(4)	111.8(2)	111.5(4)
S2–M–S3	107.8(1)	107.1(2)	107.5(1)	106.6(2)
S2–M–X	111.3(2)	111.6(4)	112.0(2)	112.2(4)
S3–M–X	110.1(2)	111.4(4)	110.4(2)	112.2(4)
B. Cl–Cu–P, Cl–Cu–S, P–Cu–S and S–Cu–S Angles				
Cl–Cu1–P3	100.2(2)	102.0(2)	99.5(1)	100.9(2)
Cl–Cu1–S1	95.2(2)	95.9(2)	95.1(1)	95.7(2)
Cl–Cu1–S2	96.4(2)	96.5(2)	95.3(1)	96.2(2)
P3–Cu1–S1	130.9(2)	132.2(2)	130.6(2)	131.5(2)
P3–Cu1–S2	118.8(2)	117.6(2)	118.6(2)	117.3(2)
S1–Cu1–S2	105.2(2)	103.7(2)	106.5(1)	105.6(2)

(continued overleaf)

TABLE III. *(continued)*

Atoms	I	II	III	IV
Cl–Cu2–P2	107.6(2)	106.7(2)	107.2(1)	106.3(2)
Cl–Cu2–S1	96.3(2)	93.0(2)	95.6(1)	93.4(2)
Cl–Cu2–S3	95.5(1)	93.6(2)	94.9(1)	92.9(1)
P2–Cu2–S1	125.0(2)	126.0(2)	124.9(2)	125.2(2)
P2–Cu2–S3	121.5(2)	123.8(2)	121.3(2)	123.1(2)
S1–Cu2–S3	103.9(2)	103.8(2)	105.2(1)	105.7(2)
Cl–Cu3–P1	106.9(2)	107.4(2)	106.0(1)	106.4(2)
Cl–Cu3–S2	103.2(2)	101.8(2)	102.8(1)	101.7(2)
Cl–Cu3–S3	100.7(2)	99.8(2)	100.8(1)	101.1(2)
P1–Cu3–S2	126.2(2)	127.8(2)	126.5(2)	127.1(2)
P1–Cu3–S3	115.0(2)	115.6(2)	114.9(2)	115.2(2)
S2–Cu3–S3	101.5(2)	100.5(2)	102.4(1)	102.4(2)
C. M–S–Cu and Cu–S–Cu Angles (M = Mo, W)				
M–S1–Cu1	72.5(1)	73.7(1)	72.4(1)	72.9(1)
M–S1–Cu2	72.9(1)	73.7(1)	72.6(1)	73.1(1)
Cu1–S1–Cu2	90.4(2)	92.0(2)	91.7(1)	92.5(2)
M–S2–Cu1	72.5(1)	73.4(1)	72.4(1)	72.9(1)
M–S2–Cu3	72.9(1)	73.5(1)	73.0(1)	73.6(1)
Cu1–S2–Cu3	84.2(2)	84.3(2)	85.3(1)	84.8(2)
M–S3–Cu2	73.4(1)	74.1(1)	73.3(1)	73.6(1)
M–S3–Cu3	73.2(1)	73.8(1)	73.0(1)	73.7(1)
Cu2–S3–Cu3	85.0(2)	87.4(2)	85.8(1)	88.1(2)
D. Cu–Cl–Cu Angles				
Cu1–Cl–Cu2	74.1(1)	75.5(1)	73.2(1)	74.2(1)
Cu1–Cl–Cu3	73.1(1)	74.9(1)	72.8(1)	73.9(1)
Cu2–Cl–Cu3	75.0(1)	76.2(1)	74.3(1)	74.9(1)
E. Mean values for the Cu–PPh_3 Units				
Cu–P–C	113.9	114.7	113.6	114.0
C–P–C	104.7	103.8	105.0	104.6
P–C–C	118.6	119.1	119.1	120.0
C–C–C	119.9	119.9	120.0	120.0[a]

[a] The phenyl rings were refined as regular hexagons with a fixed C–C distance.

completed by a terdentate MXS_3^{2-} ligand (M = Mo, W; X = S, O), coordinating via sulfur. I–IV can be described as substitution products of $[PPh_3CuCl]_4$ [23], where the MXS_3^{2-} ligand replaces one PPh_3-$CuCl_3$ moiety. Figure 1 shows an ORTEP drawing of I, including the labelling of the phenyl ring atoms.

The coordination polyhedron of the M atom is a distorted tetrahedron. The angle between the terminal S or O and the bridging S atoms is larger than the angles between the bridging atoms themselves. The three Cu atoms are not equivalent. The coordination variability ranges from a strongly distorted tetrahedron (Cu3) to a nearly trigonal planar coordination (Cu1 and Cu2) with a weak fourth Cu–Cl interaction (see Fig. 2 and Table IV). It is worth noting that the three planes defined by one P and two S atoms bound to each Cu intersect close to the Mo or W atom respectively (see Table IV).

The Cu–S distances are clearly influenced by the above mentioned different coordination of the Cu atoms. The Cu3–S distances are comparable to Cu–S bonds in other compounds with tetrahedrally coordinated Cu *e.g.* in $Cu_4[SC(NH_2)_2]_9^{4+}$ (2.30–2.42 Å) [24] or $\{Cu_4W_2S_6\}(PPh_3)_4O_2$ (2.312(3)–2.363(4) Å, not considering the Cu–S

TABLE IV. Distances (Å) of the Cu and M (M = Mo, W) Atoms from the Planes Defined by the two S and the P Atom Coordinated to Cu.

Plane	Atoms	I	II	III	IV
S1 / \\ S2 — P3	Cu1	0.294(2)	0.329(2)	0.268(2)	0.307(2)
	M	0.107(1)	0.075(1)	0.077(1)	0.060(1)
S1 / \\ S3 — P2	Cu2	0.408(2)	0.330(2)	0.384(2)	0.317(2)
	M	0.027(1)	0.048(1)	0.049(1)	0.080(1)
S2 / \\ S3 — P1	Cu3	0.551(2)	0.529(2)	0.532(2)	0.514(2)
	M	0.101(1)	0.095(1)	0.078(1)	0.063(1)

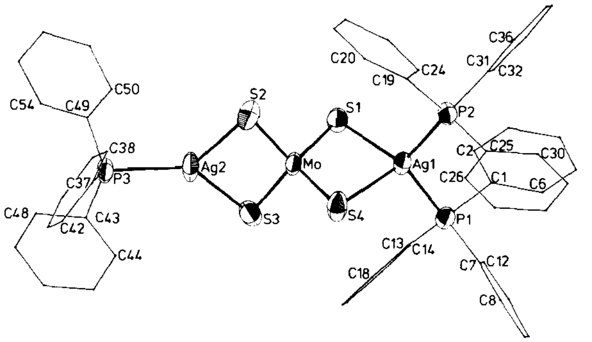

Fig. 3. Molecular structure of $(PPh_3)_3Ag_2MoS_4 \cdot 0.8CH_2Cl_2$.

bonds connecting the two symmetry related halves of the molecule [14]). The Cu1–S and Cu2–S distances, however, are significantly shorter and are close to the values observed in compounds containing trigonally planar coordinated Cu (*e.g.* in $[Cu_4(\mu_2\text{-}SPh)_6]^{2-}$ ($Cu\text{–}S_{av}$ = 2.29 Å) [25], $[Cu_5(\mu_2\text{-}SPh)_7]^{2-}$ (2.23–2.33 Å) [26] or $Cu_4[SC(NH_2)_2]_6^{4+}$ (2.19–2.31 Å) [24]). The Cu3–Cl and all Cu–P bond lengths (the latter are not influenced by the different Cu coordination) are comparable to those in $[PPh_3CuCl]_4$ (Cu–Cl = 2.363(2)–2.505(2) Å, Cu–P = 2.192(2)–2.193(2) Å) [23] while the Cu1–Cl and Cu2–Cl distances are about 0.25 Å longer than in $[PPh_3CuCl]_4$.

The monoclinic unit cells of V and VI, which are isomorphous to $(PPh_3)_3Cu_2MoS_4 \cdot 0.8CH_2Cl_2$ [27] and $(PPh_3)_3Ag_2WS_4 \cdot 0.8CH_2Cl_2$ [28], contain 4 molecules which are orientated nearly parallel to the *b* axis. Interatomic distances and bond angles are given in Table V. In V and VI a tetrahedral (distorted) MS_4^{2-} ligand (M = Mo, W) forms a bridge between two M′ atoms (M′ = Cu, Ag), one M′ atom having one, the other two PPh_3 ligands. Thus one M′ atom is tetrahedrally coordinated (distorted), the other tri-

TABLE V. Interatomic Distances and Bond Angles.

a. Interatomic Distances (Å) in V and VI with Standard Deviations.

Atoms	V	VI
A. M···M′ Distances (M = Mo, W; M′ = Cu, Ag)		
M···M′1	2.809(3)	3.030(2)
M···M′2	2.670(3)	2.860(2)
B. M–S, M′–S and M′–P Distances (M = Mo, W; M′ = Cu, Ag)		
M–S1	2.201(7)	2.195(5)
M–S2	2.217(8)	2.214(5)
M–S3	2.231(8)	2.215(5)
M–S4	2.206(8)	2.194(5)
M′1–S1	2.337(8)	2.573(4)
M′1-S4	2.328(8)	2.571(5)
M′2–S2	2.250(9)	2.460(5)
M′2–S3	2.214(8)	2.457(5)
M′1–P1	2.335(8)	2.471(4)
M′1–P2	2.279(8)	2.470(4)
M′2–P3	2.209(8)	2.380(4)
C. Mean Values for the PPh_3 Units		
P–C	1.822	1.813
C–C	1.402	1.403

b. Bond Angles (deg) in V and VI with Standard Deviations.

Atoms	V	VI
A. S–M–S Angles (M = Mo, W)		
S1–M–S2	110.2(3)	108.1(2)
S1–M–S3	110.5(3)	107.7(2)
S1–M–S4	107.6(3)	112.6(2)
S2–M–S3	106.7(3)	112.5(2)

(continued overleaf)

TABLE V. *(continued)*

Atoms	V	VI
S2–M–S4	110.1(3)	107.7(2)
S3–M–S4	111.8(3)	108.5(2)
B. S–M′–S, S–M′–P and P–M′–P Angles (M′ = Cu, Ag)		
S1–M′1–S4	99.4(3)	90.4(2)
S1–M′1–P1	105.0(3)	107.8(1)
S1–M′1–P2	115.5(3)	115.9(1)
S4–M′1–P1	110.8(3)	112.6(2)
S4–M′1–P2	105.7(3)	105.5(2)
P1–M′1–P2	118.8(3)	120.6(2)
S2–M′2–S3	106.1(3)	97.0(2)
S2–M′2–P3	123.9(3)	130.6(2)
S3–M′2–P3	130.0(3)	132.5(2)
C. M–S–M′ Angles (M = Mo, W; M′ = Cu, Ag)		
M–S1–M′1	76.4(3)	78.5(1)
M–S2–M′2	73.4(3)	75.2(2)
M–S3–M′2	73.8(3)	75.3(2)
M–S4–M′1	76.5(3)	78.5(2)
D. Mean Values for the M′–PPh$_3$ Units (M′ = Cu, Ag)		
M′–P–C	114.9	113.6
P–C–C	118.8	119.9
C–P–C	104.1	104.7
C–C–C	120.0	120.0

gonally planar. Figure 3 shows an ORTEP drawing of VI with the labelling of the phenyl ring atoms. For a more detailed discussion of the structural type of V and VI see ref. [28].

The reaction of MS_4^{2-} and MOS_3^{2-} anions (M = Mo, W) with soft cations like Cu^+, Ag^+ or Au^+ in the presence of tertiary phosphine ligands leads to the formation of different types of polynuclear compounds:

(1) Cubane-like (I–IV)

(2) Species with cages fused by two six-membered metal-sulfur rings of the formula $\{M'_4M_2S_6\}(PR_3)_4X_2$ (M′ = Cu, Ag; M = Mo, W; R_3 = Ph_3, $(C_7H_7)_3$, $MePh_2$; X = O, S) (see Fig. 4).

(3) Trinuclear ones of composition $(PR_3)_nM'_2MS_4$ (M′ = Cu, Ag, Au; M = Mo, W; R_3 = Ph_3, $MePh_2$; n = 2, 3, 4).

The compounds with n = 3 are of the same type as V and VI, while for n = 2 both M′ atoms are surrounded trigonally planar (see Fig. 4). The proposed structure for n = 4 (both M′ atoms coordinated tetrahedrally; see Fig. 4) has not yet been ascertained by single crystal structure analysis but it has been deduced from spectroscopic investigations such as ^{31}P NMR, IR, Raman, and in particular resonance Raman spectroscopy [29].

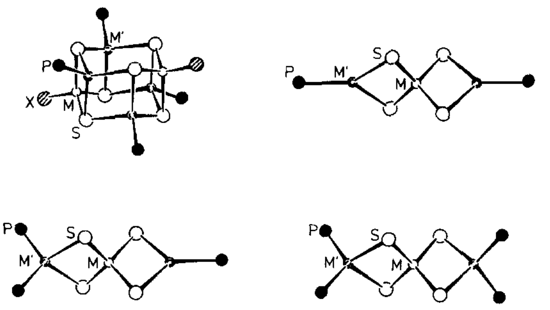

Fig. 4. Structures of $\{M'_4M_2S_6\}(PR_3)_4X_2$ and $(PR_3)_nM'_2MS_4 \cdot mCH_2Cl_2$ type compounds (M′ = Cu, Ag, Au; M = Mo, W; X = S, O; R_3 = Ph_3, $(C_7H_7)_3$, $MePh_2$; n = 2, 3, 4; m = 0, 0.8).

Table VI shows a summary of the above mentioned types of compounds together with some selected structural data.

As all the species with different structures and stoichiometry (see Table VI) have roughly similar formation tendencies, the relative concentration of the reactants is the most important factor influencing their formation. This can be illustrated by the following examples:

(a) The first types (1) and (2) of the compounds differ in their Cu:M ratio (3:1 *vs.* 2:1) (see Table VI). Either $\{Cu_3WS_3Cl\}(PPh_3)_3O$ (II) or $\{Cu_4W_2S_6\}(PPh_3)_4O_2$ [14] is obtained, depending on the relative amount of WOS_3^{2-} and $CuCl_2 \cdot 2H_2O$ used in the preparation procedure (see preparation of II and ref. [14]).

(b) $(PPh_3)_4Ag_2WS_4$ and $(PPh_3)_3Ag_2WS_4 \cdot 0.8CH_2Cl_2$ [28] can be synthesized by adding a solution of PPh_3 in CH_2Cl_2 to $\{Ag_4W_2S_6\}(PPh_3)_4S_2$.

(c) $\{Ag_4W_2S_6\}(PPh_3)_4S_2$ [12] can be prepared from $(PPh_3)_4Ag_2WS_4$ (VII) or $(PPh_3)_3Ag_2WS_4 \cdot 0.8CH_2Cl_2$ [28] by dissolving these in CH_2Cl_2 and topping the solution with n-pentane/acetone whereby 'one or two PPh_3 ligands are extracted'.

Compounds of the type (3) are not obtained using MOS_3^{2-} (M = Mo, W) but preferably cubane type species (1) (because of the preferred formation of Cu–S bonds). In this context it is interesting to note that in the case of the preparation methods for I and III the compounds V and $(PPh_3)_3Cu_2MoS_4 \cdot 0.8CH_2Cl_2$ are formed to some extent using very freshly prepared solutions of MS_4^{2-}, whereas traces of MOS_3^{2-} (formed by hydrolysis of the tetrathioanions) 'catalyze' the formation of practically pure I and III. In a few cases different species are also obtained, as mentioned above (see also [10]).

TABLE VI. Compounds in the System $M'^{+}/MXS_3^{2-}/PR_3$ (M' = Cu, Ag, Au; M = Mo, W; X = S, O; R_3 = Ph_3, $(C_7H_7)_3$, $MePh_2$).

Compounds	M':M:PR_3 Ratio	$n_{M'-S}$[a]	$n_{M'}$[b]	$M-S_{term}$[d]	$M-S_{br}$[d]	$M\cdots M'$[d]	Ref.
$\{Cu_3WS_3Cl\}(PPh_3)_3S$	3:1:3	6	3	2.131	2.251	2.717	[f]
$\{Cu_3WS_3Cl\}(PPh_3)_3O$	3:1:3	6	3	1.754[e]	2.241	2.738	[f]
$\{Cu_3MoS_3Cl\}(PPh_3)_3S$	3:1:3	6	3	2.118	2.254	2.700	[f]
$\{Cu_3MoS_3Cl\}(PPh_3)_3O$	3:1:3	6	3	1.769[e]	2.259	2.718	[f]
$\{Cu_4W_2S_6\}(PPh_3)_4O_2$	2:1:2	6	4	1.696[e]	2.251	2.780	[14]
$\{Cu_4W_2S_6\}(P(C_7H_7)_3)_4O_2$	2:1:2	6	4	1.70[e]	2.248	2.784	[30]
$\{Ag_4Mo_2S_6\}(PPh_3)_4S_2$	2:1:2	6	4	2.108	2.227	2.975	[13]
$\{Ag_4W_2S_6\}(PPh_3)_4S_2$	2:1:2	6	4	2.121	2.234	2.997	[12]
$\{Ag_4W_2S_6\}(PMePh_2)_4S_2$	2:1:2	6	4	2.131	2.225	3.002	[15]
$(PMePh_2)_2Au_2WS_4$	2:1:2	4	2	–	2.219	2.840	[31]
$(PPh_3)_3Cu_2MoS_4 \cdot 0.8CH_2Cl_2$	2:1:3	4	2	–	2.208	2.709	[27]
$(PPh_3)_3Cu_2WS_4 \cdot 0.8CH_2Cl_2$	2:1:3	4	2	–	2.214	2.740	[f]
$(PPh_3)_3Ag_2MoS_4 \cdot 0.8CH_2Cl_2$	2:1:3	4	2	–	2.205	2.945	[f]
$(PPh_3)_3Ag_2WS_4 \cdot 0.8CH_2Cl_2$	2:1:3	4	2	–	2.207	2.971	[32]
$(PPh_3)_4Ag_2MoS_4$	2:1:4	4[c]	2[c]				[33]
$(PPh_3)_4Ag_2WS_4$	2:1:4	4[c]	2[c]				[32]
$(PMePh_2)_4Ag_2WS_4$	2:1:4	4[c]	2[c]				[15]

[a] Number of M'–S bonds per MXS_3^{2-} ligand. [b] Number of M' atoms that one MXS_3^{2-} ligand is coordinated to. [c] Suggested from spectroscopic data (see text). [d] Average value. [e] M–O distance. [f] This work.

Bioinorganic Relevance

Species containing Mo and Cu are interesting because of the interrelation of both metals in biological processes (the so-called Mo–Cu antagonism [2, 7]). An *excess* of Cu is accumulated in the liver of ruminants, when the Mo concentration in the forage is low [2] and a copper *deficiency* in ruminants in many parts of the world is observed in the reverse case (secondary trace element deficiency [7]). The latter effect is synergized by dietary sulfur compounds [7]. Furthermore it has been supposed that thiomolybdates, which are probably formed in the digestive tract of ruminants, could be responsible for this [7] because they restrict the copper absorption by the intestinal tract. It has been suggested, that the formation of $CuMoS_4$ from Cu^{2+} and thiomolybdate (formed from molybdate with S^{2-} after reduction of sulfate to sulfide) could be responsible for this [3]. This is definitely incorrect, as Cu^{2+} is reduced in the presence of thiometallates like WS_4^{2-} and MoS_4^{2-} [32]. Thiomolybdates are the most effective antagonists of copper [7].

The formation of polynuclear Cu complexes with thiomolybdate ions as ligands in biological processes (whereby copper would become metabolically unavailable) must be considered as essential for the Cu–Mo interrelation, considering the fact that thiomolybdates have a high tendency to form complexes with transition metal cations, especially soft ones like Cu in the presence of other ligands. (In this context it is worthwhile mentioning the relevance of the thiomolybdate ligand to the nitrogenase problem [33]).

It is probable that Cu–Mo–S interrelationships do not only play a key role in different biological processes in plants and animals, but also in Wilson's disease in humans [2]. For most individuals the rate of elimination of Mo is proportional to that of Cu, whereby for patients having Wilson's disease the elimination rates for both metals are much higher [2].

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